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June 9, 2008

Accelerator Simulation and Theoretical Modelling of Radiation
EffectsTM-34567

Kharkov, Ukraine

June 9, 2008 through June 13, 2008

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Experimental Determination of Metal Fuel Point Defect Parameters

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Abstract: Nuclear metallic fuels are one of many options for advanced nuclear fuel cycles because they provide dimensional stability, mechanical integrity, thermal efficiency, and irradiation resistance while the associated pyro-processing is technically relevant to concerns about proliferation and diversion of special nuclear materials. In this presentation we will discuss recent success that we have had in studying isochronal annealing of damage cascades in Pu and Pu(Ga) arising from the self-decay of Pu as well as the annealing characteristics of non-interacting point defect populations produced by ion accelerator irradiation. Comparisons of the annealing properties of these two populations of defects arising from very different source terms are enlightening and point to complex defect and mass transport properties in the plutonium specimens which we are only now starting to understand as a result of many follow-on studies. More importantly however, the success of these measurements points the way to obtaining important mass transport parameters for comparison with theoretical predictions or to use directly in existing and future materials modelling of radiation effects in nuclear metallic fuels. The way forward on such measurements and the requisite theory and modelling will be discussed. *We bring to the attention of the reader that this article is based wholly or in part on earlier publications of the authors.*

1. Background

The physical metallurgy of δ -phase plutonium, particularly those aspects related to radiation damage and associated vacancy and self-interstitial properties, is technologically important, and yet still requires a deeper fundamental understanding. Low-temperature damage-accumulation, and subsequent isochronal-annealing provide an experimental methodology for determining important mass transport parameters based on chemical rate equations, e.g., the interstitial migration energy and the vacancy migration energy [1]. The starting point for deducing these parameters is the ability to perform high fidelity annealing experiments. Although annealing experiments have been reported for δ -stabilized Pu(Al) [2, 3], the fidelity of the data was limited, and hence the analyses were only qualitative. Previously we reported high-fidelity isochronal-annealing curves of the damage induced electrical resistance for self- and proton-irradiated Pu(Ga)[4]. The annealing properties were measured on δ -stabilized alloy, Pu(3.3 at%Ga), an *fcc* δ -phase of plutonium which was resistant to the martensitic phase transformation to the α' -phase at all temperatures of these experiments. An important element of the earlier work was the experimental determination of the temperature for the various annealing Stages I to V.

2. Damage Accumulation and Annealing in δ -Phase Pu(Ga)

We measured, as near to the dilute limit as was practical, the temperature dependence of the resistance of radiation damage of defect ensembles or

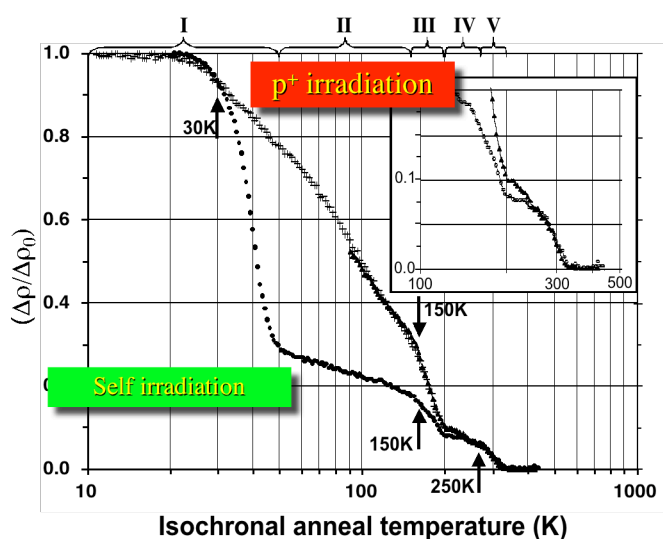


Fig. 1: Isochronal annealing curves for Pu(3.3 at% Ga) irradiated with self-decay and with protons. The isochronal time was 300 sec.

	T_m (K)	T_I (K) measured	T_I (K) (0.02 ± 0.015) T_m predicted	T_{III} (K) measured	T_{III} (K) (0.2 ± 0.02) T_m predicted	T_V (K) measured	T_V (K) (0.45 ± 0.03) T_m predicted
Pb	601	4	12 ± 9	160	120 ± 12	290	270 ± 18
Al	933	37	19 ± 14	220	187 ± 19	----	420 ± 28
Pu(Ga) 3.8MeV p^+	953	~ 35	19 ± 14	180 ± 5	191 ± 19	310 ± 5	429 ± 29
Pu(Ga) α -decay	953	45 ± 5	19 ± 14	180 ± 5	191 ± 19	310 ± 5	429 ± 29
Ag	1235	28	25 ± 20	230	247 ± 25	540	556 ± 37
Au	1337	----	27 ± 20	290	267 ± 27	530	602 ± 40
Cu	1356	38	27 ± 20	250	271 ± 27	605	610 ± 41
Ni	1726	56	35 ± 26	340	345 ± 35	750	777 ± 52

Table 1: Empirical estimates for Stage I, Stage III, and Stage V transitions as a function of the melting temperature T_m [5]. The annealing data for Pu(3.3at%Ga) with a 300s isochronal anneal is shown. Stage I for the p^+ irradiation of the Pu(Ga) is not clear but appears to be ~ 35 K. For the other Stages statistical errors are indicated. Longer anneal times will shift the transitions to lower temperatures, but no more than ~ 10 K.

populations produced by low-temperature damage-accumulation and subsequent annealing [4]. Fig. 1 shows the isochronal data for self-irradiation damage accumulation and for proton irradiation. We note that while the proton irradiation appears to be typical of an annealing curve for a dirty alloy, with no clear indication of interstitial annealing stages, the self-irradiation annealing curve is strongly structured showing a modified Stage I, a Stage II and Stages III to V for vacancies. It is interesting to compare the annealing curves with empirical estimates for other metals given by Ehrhart [5] that we show in Table 1. We note that the largest difference between experiment and empirical estimates is for Stage V, the temperature where vacancy clusters become unstable. We also note that with respect to vacancies Stages III to V are indistinguishable with regards to the origin of the damage, self-irradiation or protons.

Effective activation energies can be deduced from annealing data by varying the rate, α , or time interval for the annealing while determining the transition temperature, T . Fig. 2 illustrates the result of such an experiment showing the shift in the annealing curve to higher T with shorter annealing time. Here the damage accumulation time was 5 days and the two anneal times were 100s (blue points) and 300s (pink points). The formula for extracting the activation energy, E , is:

$$\ln\left(\frac{\alpha_2 T_1^2}{\alpha_1 T_2^2}\right) = \frac{E}{k} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (1)$$

The following activation values were deduced: Stage I 0.05 to 0.1 eV, Stage III 0.5 eV, and Stage V 1.0 to 1.3 eV.

During this study we discovered that the specific resistivity for vacancies and vacancy clusters was exponentially temperature dependent. Fig. 3 shows the relevant data. Here we show the temperature dependence of the resistance for three vacancy defect populations that were produced via damage accumulation at 10K for 5 days followed by annealing at 30K 150K, and 250K. This result is a spectacular violation of Matthiessen's rule [6, 7] for vacancy-defects in δ -stabilized Pu(3.3 at%Ga) and suggests a Kondo-like impurity behaviour for

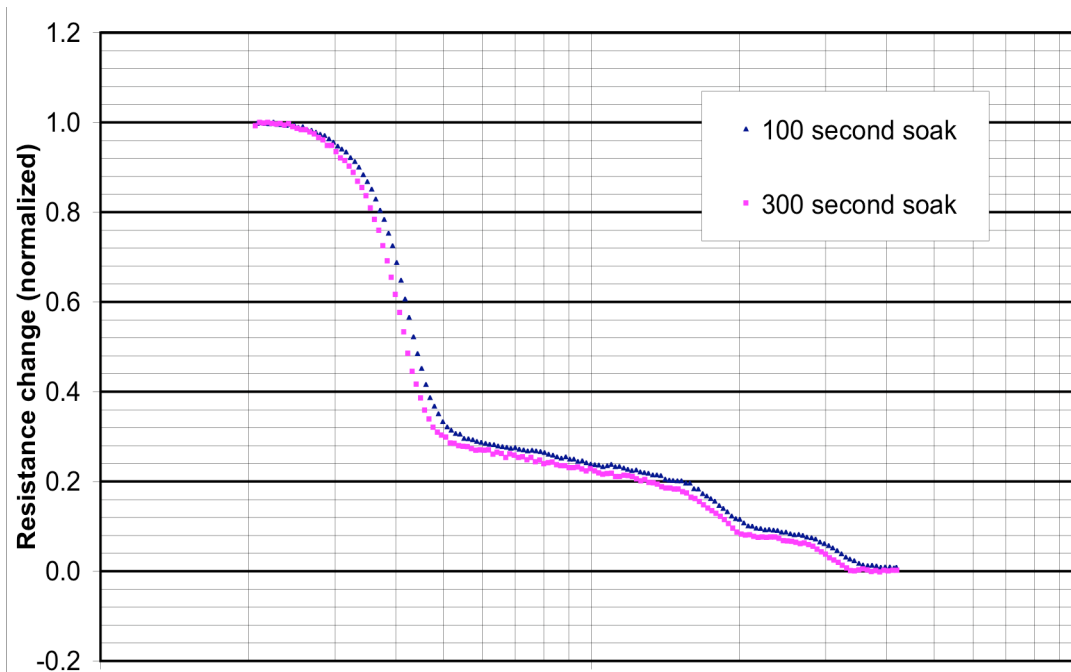


Fig. 2: Two isochronal annealing curves, 100s and 300s annealing times for each point used to deduce activation energies.

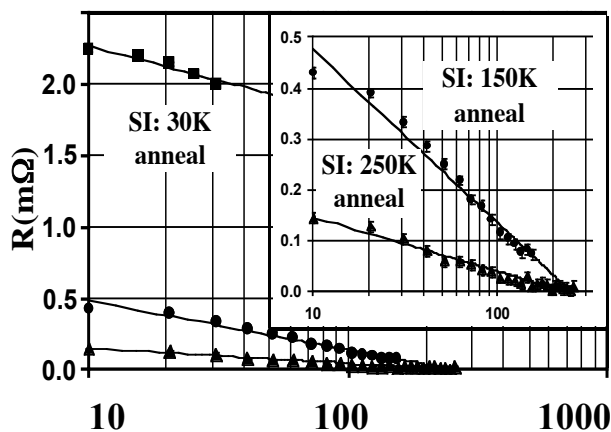


Fig. 3: The resistance for the three defect-populations resulting from self-irradiation (labeled SI:) of Pu(Ga) at $T=10\text{K}$ for 5d and then annealed successively at $T_i=(30\text{K}(\blacksquare), 150\text{K}(\bullet), \text{ and } 250\text{K}(\blacktriangle))$ for 1h prior to measuring the plotted resistance data at a set of temperatures, T_j . The $T(\text{K})$ axis refers to the T_j values of the data points. The inset shows the same data for the self-irradiations at 150 and 250K where the common $\ln(T)$ axis intercept is evident and the systematic deviation of the data points at 10K is seen.

vacancies in this system. As a result of this observation we moved to magnetization studies of self-damaged Pu and Pu-alloys

3. Emergence of Magnetism Due to Disorder

Despite the importance of the $5f$ electrons in defining structure and physical properties of Pu, there is no experimental evidence that these electrons localize to form magnetic moments in pure Pu. Instead, a large temperature-independent Pauli susceptibility indicates that they form narrow conduction bands. We have shown previously that radiation damage from the alpha-particle decay of Pu creates numerous defects in the crystal structure, which produce a significant temperature-dependent magnetic susceptibility, $\chi(T)$, in both α -Pu and δ -Pu (stabilized by 4.3 at% Ga) [8]. This effect is reversible by thermal annealing above room temperature. The magnetic and resistive annealing curves for the α - and δ -Pu are shown in

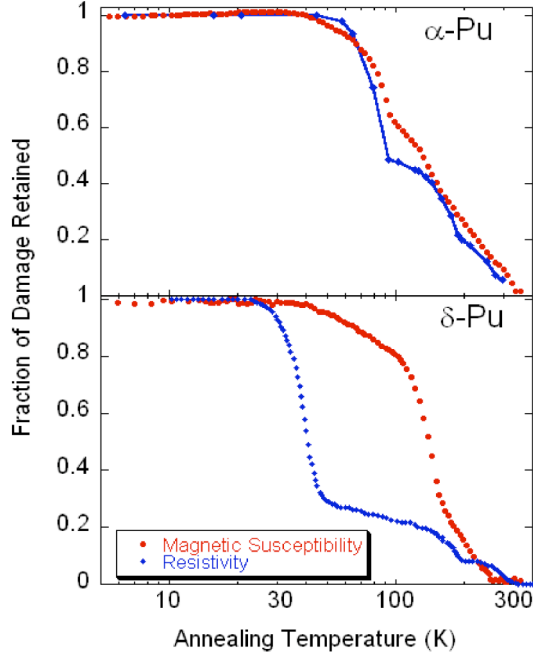


Fig. 5: Isochronal annealing curves for α -Pu and Ga stabilized δ -Pu illustrating that damage is frozen in place below ~ 30 K. The red circles are the magnetic susceptibility measurements from reference [8] while the blue diamonds are resistivity data taken from references [3] and [4] respectively

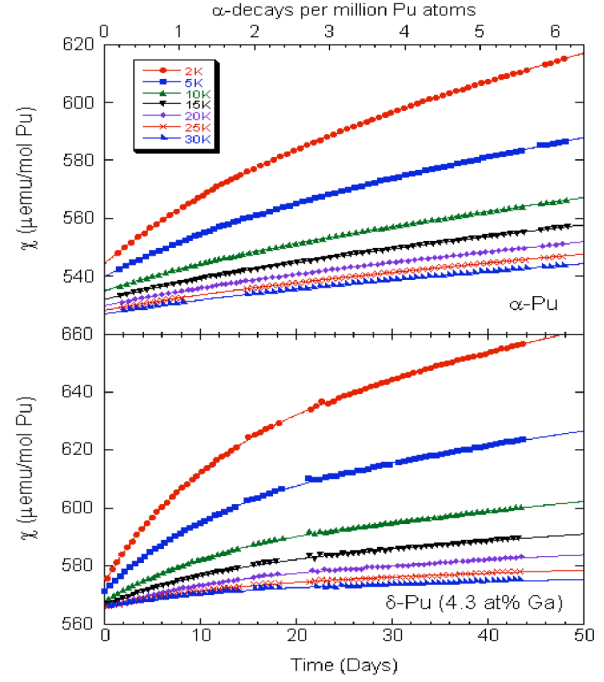


Fig. 4: Representative isothermal magnetic susceptibilities for α -Pu and δ -Pu (4.3 at% Ga) plotted as a function of time (number of α -decays). The lines are fits to Eq. (1) described in the text.

Fig. 5 and Fig. 4. The reader should note that while the annealing curves for resistive and magnetically tracked annealing in α -Pu are quite similar, the corresponding curves for Ga stabilized δ -Pu are quite different with regards to the first annealing stage, the stage associated with interstitial mobility. This suggests that while in the monoclinic α -Pu both interstitials and vacancies contribute to the magnetization, in the more open *fcc* δ -Pu lattice vacancies dominate.

Fig. 5 illustrates that below 35 K, the radiation damage is “frozen” in place, permitting the evolution in time and temperature ($T < 35$ K) to be studied systematically. By accumulating damage over a sufficiently long time while measuring the susceptibility, χ as a function of temperature, T , we could produce susceptibility isotherms for the α -Pu and for the δ -Pu. These isotherms are described by a single formula with one materials dependent variable, the time constant τ .

$$\chi(t, T) = \chi_i(T) + \chi_v(T)(1 - e^{-t/\tau}) + \chi'_D(T)t \quad (2)$$

Thus, we deduced that self-damage creates localized magnetic moments in previously nonmagnetic plutonium. While Eq. 2 may not be a unique description of the data in Fig. 1 it allows us to deduce the dimensional nature of the disorder induced magnetism. The parameter, τ , represents, in the context of Eq. 2, a spherical volume around the damage cascade produced by the U recoil that, because of disorder, exhibits an effective magnetization. We determined that this volume includes many more atoms (500,000) than are displaced by the damage cascade (3000).

4. Lattice Expansion with Am

Plutonium and its simple binary alloys are known to be extremely sensitive to impurities, defects, and particularly disorder. In earlier work we have added disorder by alloying plutonium with americium, $\text{Pu}_{1-x}\text{Am}_x$, forming a stable fcc phase (δ -Pu, β -Am) from $0.06 < x < 0.80$ where the lattice parameter increases with x [9]. The electronic structure of americium is $5f^6$, thus it has a $J=0$ ground state and its magnetic susceptibility is primarily due to a large Van Vleck contribution [10]. Being a single ion effect this should be independent of the local environment and thus should be insensitive to radiation damage. Thus any changes observed in the magnetic susceptibility of the PuAm alloys that deviate from a simple linear combination of the two end members should reflect a change in the magnetic properties of the plutonium. Preliminary results indicate that the expanding of the lattice as a function of Am concentration (negative pressure) results in a tendency of the temperature dependent partial susceptibility for the Pu sub-lattice which is indicative of spin fluctuations.

Another method for adding disorder is through the radioactive decay of Pu and Am which produces a ~ 5 MeV α -particle and a corresponding recoil (U or Np) that creates a large number of vacancies and interstitials, of which a substantial fraction, after relaxation, remain frozen in place at low temperatures. Disorder from self-damage increases with time and is observable through magnetic susceptibility measurements, where Curie Weiss behavior evolves and thus demonstrates the creation of local magnetic moments. These emergent moments may be removed by thermal annealing, proving they arise from the disorder created by vacancies and interstitials. Radiation damage studies on $\text{Pu}_{1-x}\text{Am}_x$ alloys thus allow investigation of how inherent chemical disorder and structural disorder each influence the behavior of the electronic structure of plutonium. In Fig. 6 we observe accumulating magnetization for a suite of Pu(Am) alloys as well as for Pu and Pu(Ga). The data is plotted against alpha decays per (Pu+Am) atoms. While there is a trending in the data, what

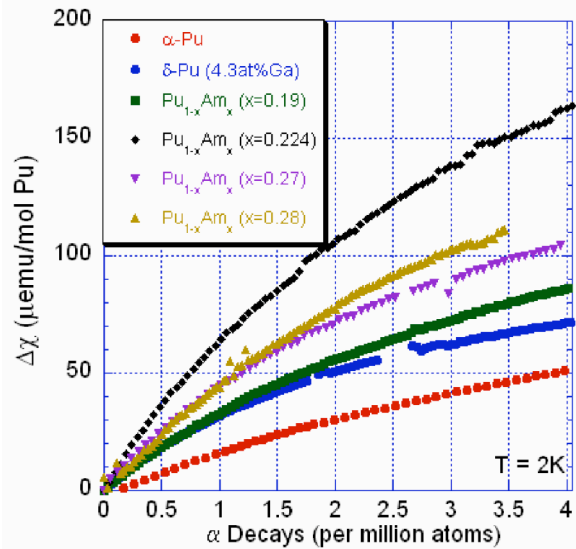


Fig. 6: Increase in magnetic susceptibility per mol Pu due to self damage accumulated at low temperatures. Apart from the 22.4% Am specimen, the effect increases with increasing lattice constant. The curvature as a function of damage suggests this effect is saturating.

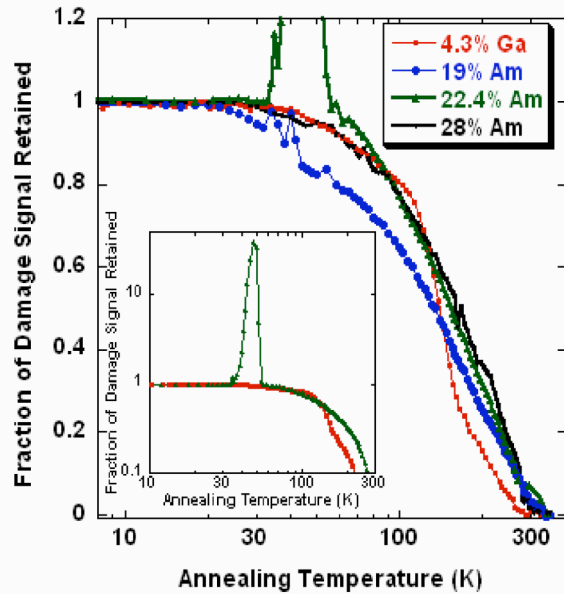


Fig. 7: Isochronal annealing curves for delta phase Pu specimens. The distinct features of the 4.3at% Ga stabilized phase are smeared out in the $\text{Pu}_{1-x}\text{Am}_x$ alloys. The 22.4% Am alloy shows a remarkable increase in magnetization near Stage I, that is more clearly illustrated on a log scale in the inset. Similar but less dramatic features are observed in the 19% Am alloy. This “reverse annealing” may be indicative of a damage induced metastable phase.

stands out is the much larger response of the 22.4 % Am alloy. Careful annealing studies reveal a new low temperature phase heretofore unknown.

In alloys, as opposed to intermetallic compounds, the distinct phases of annealing may be smeared out due to the disorder inherent in the system. This is shown in Fig. 4 where the distinct stages observed in the Ga-stabilized δ -Pu are no longer readily extracted from the PuAm alloy curves. A second feature, abundantly clear in the 22.4% Am specimen is an anomalous increase in the signal retained with increasing temperature, where the signal grows to $\sim 40\times$ the initial damage signal near the temperature where Stage I annealing takes place in other alloys. This is illustrated in the inset of Fig. 7, where the “fraction of damage signal retained is shown on a log-log plot along with the Ga-stabilized Pu specimen. The 19% Am curve shows a similar tendency beginning at roughly the same temperature, although it is much less dramatic. In the simple picture of annealing out damage, the curve should monotonically decrease for each higher temperature since less damage is retained after successive anneals. Small increases in annealing curves have been observed previously [11] for several other alloys such as Cu_3Au , where the increase in signal was termed “reverse annealing”. One explanation for such behaviour is that the radiation damage is either disordering an ordered intermetallic system, or creating small ordered regions in an otherwise disordered system.

5. Conclusion

We have outlined defect accumulation and annealing experiments conducted on Pu, Pu(Ga) and Pu(Am) over several years. Our purpose was to illustrate to the reader that important defect properties of Pu and Pu alloys are experimentally accessible. However, and even more importantly we wish to caution that there are complexities associated with the solid-state physics of Pu and to a larger extent the 5f series, and these complexities can and do affect the defect properties. Most importantly magnetism plays an important role in disordered Pu and Pu alloys and must be taken into account when considering defect properties, mass transport and phase stability.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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